AD

AD-E402 981

Technical Report ARWEC-TR-03004

STRUCTURAL FEATURES OF 2-NITROGUANIDINE

A. J. Bracuti

June 2003

US ARMY
TANK AUTOMOTIVE AND
ARMAMENTS COMMAND
ARMAMENT RDE CENTER

U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND ENGINEERING CENTER

Warheads, Energetics & Combat-support Armament Center

Picatinny Arsenal, New Jersey

Approved for public release; distribution is unlimited.

20030624 037

The views, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

The citation in this report of the names of commercial firms or commercially available products or services does not constitute official endorsement by or approval of the U.S. Government.

Destroy this report when no longer needed by any method that will prevent disclosure of its contents or reconstruction of the document. Do not return to the originator.

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-01-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden to Department of Defense, Washington Headquarters Services Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (*From – To*)
June 2003		

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
STRUCTURAL FEATURES OF 2-NITROGUANIDINE	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHORS	5d. PROJECT NUMBER
A. J. Bracuti	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
ARDEC, WECAC Energetic and Warheads Division (AMSTA-AR-WEE) Picatinny Arsenal, NJ 07806-5000	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
ARDEC, WECAC Information Research Center (AMSTA-AR-WEL-TL) Picatinny Arsenal, NJ 07806-5000	11. SPONSOR/MONITOR'S REPORT NUMBER(S) Technical Report ARWEC-TR-03004

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The crystal and molecular structure of solid nitroguanidine (NQ) was refined using x-ray single-crystal diffraction methods. Previous structure determinations yielded values for the imino C-N bond that either equaled or exceeded the amino C-N single bond lengths, but these data were neither precise nor particularly accurate. This study was undertaken to obtain more precise and accurate structural parameters. The experimental structural parameters of crystalline NQ are compared to the theoretical structural parameters of the isolated NQ molecule. This investigation confirms that the C-N bond anomaly was real. However, it is concluded that the anomaly in the C-N bonds in crystalline NQ is a result of the strong intermolecular hydrogen bond forces and to a lesser extent the intermolecular forces in the NQ crystal structure. It is also concluded that these same intermolecular hydrogen bond forces are responsible for the enhanced insensitivity of NQ to impact.

15. SUBJECT TERMS

Nitroguanidine (NQ) Isolated nitroguanidine molecule Structure Crystal Impact sensitivity

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			A. J. Bracuti
U	U	U	SAR	16	19b. TELEPHONE NUMBER (Include area code) (973) 724-5759

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

CONTENTS

	Page
Introduction	1
Experimental	2
Results and Discussion	2
Conclusions	8
Recommendations	8
References	11
Distribution List	13

TABLES

1	Crystallographic data	9
2	Atomic coordination and Beq/Biso	9
3	Hydrogen bond lengths in Angstroms (Å) and bond angles in degrees (deg)	9
4	Comparison of x-ray bond data for crystalline NQ with theoretical** bond data for isolated NQ molecule	10
5	C-N bond in isolated guanidine and NQ molecules and crystalline NQ	10
6	Comparison of N-N bond lengths and bend angles in the isolated NQ molecule, crystalline NQ, and crystalline RDX	10

INTRODUCTION

Although nitroguanidine (NQ) has been used in explosive and propellant formulations for many years, some questions still remain concerning the structure of this energetic molecule.

The parent of NQ, the guanidine molecule $(NH2)_2C(NH)$, is a very strong base, that has two amino groups and one imino group. Hence, nitro group substitution is possible on either the imino nitrogen atom (symmetric nitrimine) or on either one of the two amino nitrogen atoms (asymmetric nitramine).

In 1982, Thiele (ref. 1) concluded from chemical data that the asymmetric nitramine was the correct molecular conformation. This view was widely held by chemists until 1951, when McKay et al (ref. 2) presented evidence for the symmetric nitrimine form.

In 1956, Bryden et al (ref. 3) undertook a single-crystal structure determination using visual intensity estimates of Weisenerg photographs, in which only heavy atom positions were located. In contrast to the Thiele nitramine model, Bryden concluded from the x-ray data that solid NQ exists as the symmetric nitrimine.

Bryden reported three apparently equivalent C-N distances with values of 1.32(2) Å for the imino group and 1.35(2) and 1.34(1) Å for the respective amino groups. The apparent C-N bond equivalence was attributed to resonance between eight statistically weighted valence-bond hybrids. Today, this would be described as total delocalization of the imino group's pi-electrons.

However, it could also be rationally argued that his apparent C-N bond-length equivalence is actually an aberration caused by the limitation of Bryden's two-dimensional photographic data. Since these limited data resulted in bond distances that were determined only to the second decimal place with an average estimated standard deviation of ±0.01 Å, small but real differences in actual bond lengths would not be detectable.

In 1981, Choi (ref. 4) conducted a neutron powder-diffraction study in which, unlike the original photographic x-ray determination, hydrogen atom positions as well as heavy atom positions were determined. The neutron data corroborated that solid NQ exists as the symmetric nitrimine rather than the asymmetric nitramine.

Although both the original x-ray and neutron diffraction studies yielded similar molecular conformations for NQ, differences in respective selected bond lengths were observed. In contract to the x-ray data, the neutron bond distances were measured to the third decimal place, but with large standard deviations.

As expected, the more comprehensive neutron diffraction data revealed that the three C-N bonds are, in fact, not equivalent. However, the neutron data did not improved agreement with accepted values for C-N bond types. Instead, it made matters worse, because now the reported imino C-N bond [1.359(9) Å] is significantly longer than either one of the amino C-N bonds [1.330(8) Å and 1.309(7) Å]. Normally, the imino C-N bond is a double bond that uses sp^2 bonding and is shorter than the amino C-N single bond that uses sp^3 bonding. However, in this

case the apparent bond order of each amino C-N bond is greater than that of the imino C-N bond. The magnitudes of these bond lengths suggest that each bond is a partial double bond with greater but not equivalent pi-electron localization in the two amino C-N bonds.

In 1986, the NMR study by Bulusu (ref. 5) also confirmed that NQ exists only as a nitrimine in both the solid state an in solution. Although it has been conclusively established that solid NQ exists exclusively as the symmetric nitrimine, the reason for the abnormal elongation of the imino C-N bond remained unresolved.

This laboratory initiated a single-crystal x-ray diffraction study in an effort to both obtain better bond distance values and to resolve or explain the apparent bond-length anomaly.

EXPERIMENTAL

A transparent prism of NQ having approximate dimensions of 0.25 x 0.28 x 0.30 mm was mounted on a glass fiber that was inserted on a diffractometer connected to a RAXIS-IIC plate detector. All diffraction data were collected at 20±1°C.

Heavy atom positions were determined with direct methods and all hydrogen atom positions were located by means of difference Fourier techniques. Heavy atoms were refined anisotropically with full-matrix least squares analysis and the hydrogen atoms were refined isotropically.

The molecular geometry of an isolated NQ molecule was optimized with the ab initio SCF method using 6G31** basis sets for all atoms using the quantum mechanics program packaged HyperChem5.1 (ref. 6)

RESULTS AND DISCUSSION

Pertinent crystallographic data and atomic coordinates with equivalent temperature factors are presented in tables 1 and 2, respectively. Hydrogen bond data are presented in table 3. X-ray bond data and theoretical bond data for the NQ are compared in table 4. A comparison of the C-N bond data for crystalline NQ and the isolated guanidine and NQ molecules are presented in table 5. Table 6 lists N-N bond data for an isolated NQ molecule, crystalline NQ, and crystalline cyclotrimethylenetrinitramine (RDX). The molecular packing of NQ (with hydrogen bond network) viewed down the c axis of the unit cell is presented in figure 1, and the NQ molecule with its atom numbering scheme is presented in figure 2.

Nitroguanidine crystallizes in the non-centrosymmetric orthorhombic space group Fdd2 (#43). The unit-cell parameters (table 1) are a = 17.6390(5) Å, b = 24.87307(7) Å, and c = 3.5909(1) Å, and $\alpha = \beta = \gamma = 90$ deg. Sixteen NQ molecules are located at the 16 general positions:

1. (X, Y, Z)
2. (-X, -Y, Z)
3. (¼-X, ¼+Y, ¼+Z)
4. (¾+X, ¾-Y, ¼+Z)
5. (X, ½+Y, ½+Z)

6. (-X, ½-Y, ½+Z)
7. (¼-X, ¾+Y, ¾+Z)
8. (¾+X, ¼-Y, ¾+Z)
9. (½+X, Y, ½+Z)
10. (½-X, -Y, ½+Z)
11. (¾-X, ¼+Y, ¾+Z)
12. (¼+X, ¾-Y, ¾+Z)
13. (½+X, ½+Y, Z)
14. (½-X, ½-Y, Z)
15. (¾-X, ¾+Y, ¼+Z)
16. (¼+X, ¼-Y, ¼+Z)

The crystal structure depicted in figure 1 consists of an infinite three-dimensional network of hydrogen-bonded chains of NQ molecules. Each NQ molecule has four donor hydrogen atoms that form six hydrogen bonds with two acceptor oxygen atoms and one acceptor nitrogen atom. The hydrogen bond data in table 3 indicate that the H(4) atom forms bifurcated hydrogen bonds consisting of one intra-molecular hydrogen bond with the O(1) atom [N(2)-H(4)...O(1), 2.594(2) Å], and one intermolecular hydrogen bond [N(2)-H(4)...O(1), 3.040(2) Å] with O(1) atom of an adjacent NQ molecule. The H(2) atom forms bifurcated intermolecular hydrogen bonds [N(1)-H(2)-O(2), 2.950(2) Å] and [N(1)-H(2)-O(2), 2.962(2) Å] with the O(2) atoms of two different adjacent NQ molecules. The H(1) atom also forms an intermolecular hydrogen bond [N(1)-H(1)...O(1), 3.292(2) Å] with the O(1) atom of a neighboring NQ molecule. The H(3) atom forms an intermolecular hydrogen bond [N(2)...H(3)-N(3), 3.137(3) Å] with the N(3) atom of a neighboring NQ molecule. This infinite three-dimensional hydrogen bond network stabilizes the molecules in the crystal structure.

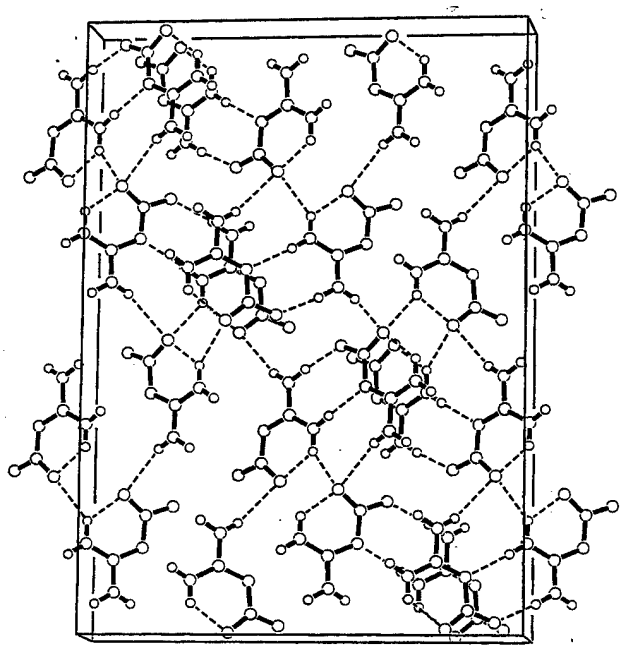

Figure 1
Nitroguanidine unit cell viewed down the c axis
(The intermolecular hydrogen bond network represented by dashed lines.)

The x-ray molecular structure in this investigation (fig. 2) generally agrees with the neutron powder diffraction molecular structure (ref. 1) in that the nitro group is substituted solely on the imino nitrogen atom [N(3)].

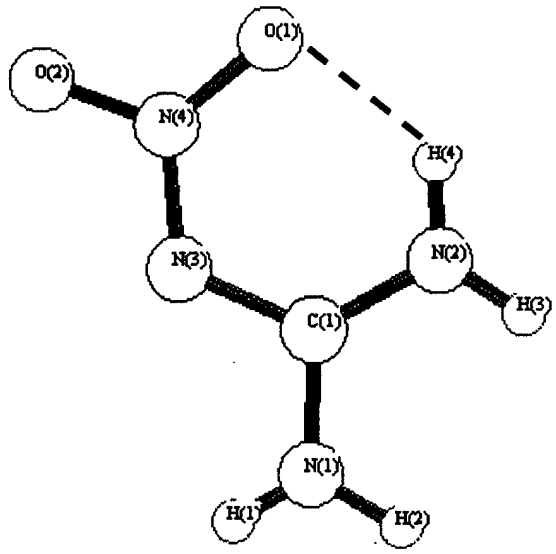

Figure 2
NQ molecule with atom number scheme and intra-molecular hydrogen bond represented by a dashed line

The amidine moiety of NQ ($N{=}CN_2$) in both structures (table 4) has amino C-N bonds that are shorter than the accepted C-N single bond length [1.472(5) Å]. The shortened amino C-N bonds suggest the pi-electrons of the imino C-N double bond are de-localized over all the C-N bonds to form partial double bonds. Although each C-N bond is a partial double bond in both models, the imino C-N bond is actually longer than either one of the amino C-N bonds.

The substitution of the electron withdrawing nitro group on the amidine moiety ehances the de-localization of the imino C-N bond pi-electrons and increases the localization of pi-electrons on the N-N nitromino bond. The N-N bond is 1.334(2) Å in the x-ray structure and 1.352 Å in the neutron structure. However, both N-N bonds are shorter than the accepted N-N single bond length [1.44(4) Å], but they are longer than the accepted value for the N-N double bond [1.25(1) Å].

The atoms in the amidine moiety are co-planar with a mean deviation of 0.002(6) Å from the amidine least squares plane. The N(2) atom has the greatest deviation of –0.004(3) Å from the plane. The planar amidine moiety is also asymmetric with respect to three non-equivalent C-N bond angles [N(2)-C(1)-N(3) 127.9(2) deg, N(1)-C(1)-N(2) 119.3(2) deg, and N(1)-C(1)-N(3) 112.8(2) deg]. A similar distribution of non-equivalent bond angles is also observed in the asymmetric amidine moieties of triaminoguanidine (ref. 7) and N-methyl-N'-nitroguanidine (ref. 8).

The least squares plane of the nitrimino moiety [N(3)-N(4)-O(1)O(2)] has a mean deviation of 0.008 Å. The N(4) atom lies the greatest distance off the least-squares plane of the nitrimino moiety [0.018(2) Å]. The N(3)-N(4) bond is bent 1.95 deg off the amidine plane and the nitro group is twisted 2 deg out of the amidine plane. These deviations, however, are small enough to consider this moiety planar. This tetrad of atoms is also asymmetric with N(3)-N(4)-O(1) equal to 124.6(1) deg, while N(3)-N(4)-O(2) and O(2)-N(4)-O(1) have values of 115.2(1) deg and 120.1(1) deg, respectively.

The heavy atoms of NQ are essentially co-planar with a mean deviation of 0.027 Å from the NQ least-squares molecular plane. The N(2) atom has the greatest heavy atom deviation of –0.066(3) Å, and the H(4) atom has the greatest hydrogen atom deviation of –0.109 Å from the least squares NQ molecular plane. The combination of shortened bond lengths, small bend and twist angles, and molecular planarity suggest that sp^2 bonding is dominant in the NQ molecule.

As with all x-ray data, the greatest uncertainty lies in the positions of hydrogen atoms. Withing the uncertainty of the torsion angles data (estimated standard deviation of ±0.021 Å between respective sets of amino C-N bonds. Furthermore, the imino C(1)-N(3) bond in this investigation is 1.372(2) Å, which is 0.013 Å longer than reported in the neutron structure [1.359(9) Å].

The breaking of the N(3)-N(4) bond is probably the critical initial step in the decomposition of NQ. This critical N(3)-N(4) bond is shortened in both the neutron and x-ray structures, but the shortening is more pronounced in the x-ray structure where the N-N bond is 1.334(2) Å as opposed to the 1.354(6) Å reported in the neutron structure. Although both structures suggest that N(3)-N(4) is a partial double bond, greater N-N double-bond character is indicated by the x-ray data.

The N-O bond lengths generally agree with bond lengths usually found in nitro-substituted organic molecules [1.22(5) Å]. The N(4)-O(1) bond length [1.247(3) Å], however, is 0.007 Å longer than N(4)-O(2) [1.239(2) Å]. This slight elongation of N(4)-O(1) may be caused by differences in hydrogen bond interactions associated with each oxygen atom. The neutron structure exhibits a similar but more pronounced difference in the respective N-O bond lengths [N(4)-O(1) is 1.261(8) Å and N-(4)-O(2) is 1.227(9) Å].

Since NQ is essentially planar and all the heavy atoms are partial double bonds, this indicates extensive sp^2 bonding. This molecular configuration should effectively stabilize the molecule as well as the critical N-N bond of the nitramino group.

Both Vladimiroff (ref. 9) and the author independently calculated with ab initio methods bond lengths in an isolated NQ molecule. In both cases, the amidine moiety is planar and all the C-N bonds (table 4) are partial double bonds. The pi-electrons are de-localized over all the heavy atoms, but apparently not to the same extent as in crystalline NQ. The amino C-N bonds in the isolated NQ molecule (1.332 Å and 1.357 Å) are longer than their counterparts in the NQ crystal [1.322(2) Å and 1.321(2) Å]. Also, the imino C-N bond in the isolated NQ molecule at 1.310 Å is 0.062 Å shorter than it is in crystalline NQ [1.372(3) Å]. Although the heavy atoms are co-planar, the hydrogen atoms with sp^3 pyramidal bonding are displaced from the amidine plane.

The N-N bond in the isolated molecule is 1.354 Å and in crystalline NQ it is 1.334(2) Å. This N-N bond shortening is attributed to double bond conjugation of amino nitrogen unshared p-type electrons with the nitro group electron system. The enhanced shortening of the N-N bond in the crystal is attributed to hydrogen bond forces in the crystal.

Pi-electron de-localization lengthens double bonds and shortens single bonds. Complete de-localization would make the three C-N bonds dimensionally equivalent. Since the C-N bonds in the isolated NQ molecule are not equivalent, pi-electron de-localization is not complete.

However, then for the imino C-N bond to be significantly longer than either amino bond, as is observed in crystalline NQ, phenomena other than pi-electron de-localization must cause the enhanced elongation of the imino C-N bond. Therefore, intermolecular interactions resulting from the molecular packing in the crystal must be responsible for the enhanced elongation of the N-N bond.

Caminiti et al (ref. 10) using ab initio molecular orbital calculations also found that for an isolated guanidine molecule N-imino substitution with an electron withdrawing functional group, such as the cyano group (C≡N), increases pi-electron de-localization in the amidine moiety. This substitution results in an amidine moiety with an elongated imino C-N double bond, shortened amino C-N single bonds, and a shortened cyano C-N single bond.

The bond data listed in table 5 demonstrate that substitution of the nitro group on the imino group of the amidine moiety has the same effect on C-N bond as does the cyano group. The two amino C-N bonds in the isolated guanidine molecule are 1.385 Å and 1.383 Å, and the imino C-N bond is 1.260 Å. Upon substitution of the nitro group on the imino nitrogen atom to form NQ, the amino C-N bonds are shortened from 1.383 Å to 1.332 Å and from 1.385 Å to 1.334 Å, respectively. The imino C-N bond is elongated from 1.260 Å to 1.310 Å, and the newly formed N-N bond is a shortened single N-N bond (1.335 Å).

Furthermore, Caminiti modeled the crystalline cyanoguanidine by assuming there are clusters of hydrogen-bonded cyanoguanidne molecules (crystal model). The forces exerted by the intermolecular hydrogen bonds further lengthen the imino C-N partial double bond, while simultaneously further shortening both amino C-N partial double bonds. The imino C-N bond of the cyano group, which is analogous to the N-N bond in NQ, is also shortened. The data shown in table 5 are consistent with the bond trends found in cyanoguanidine. The N-N bond is shortened from 1.352(2) Å, respectively. The imino C-N bond is elongated from 1.310 Å to 1.372(3) Å, while the two amino C-N bonds are shortened to 1.322(2) Å and 1.321(2) Å.

It would be informative to compare the respective bonds in the amidine moiety in both crystalline guanidine and the isolated guanidine molecule with those of the amidine moiety in the isolated NQ molecule; and in crystalline NQ. Unfortunately, the x-ray structure of crystalline guanidine has never been determined because it is too unstable. However, triaminoguanidine (TAG) should serve as an approximate substitute for crystalline guanidine, because the TAG amidine moiety is substituted with three electron-donating NH_2 groups rather than with a single electron withdrawing NO_2 group.

The amidine moiety in the isolated guanidine molecule has three asymmetric C-N bonds, with an imino C-N bond of 1.260 Å and two equivalent amino C-N bonds of 1.383 Å and 1.385 Å. The magnitudes of these bond lengths suggest that there is less pi-electron de-localization in

the amidine moiety of the isolated guanidine molecule than there is in the NQ isolated molecule. The amidine moiety in the isolated TAG molecule also has three asymmetric C-N bonds, but in this case, the imino C-N bond is only elongated to 1.276 Å and two equivalent amino C-N bonds are shortened to 1.362 Å and 1.373 Å, respectively. This indicates that pi-electron de-localization in the amidine moiety in the isolated TAG is less than in NQ, but is greater than found in guanidine.

The crystalline TAG amidine moiety also has three non-equivalent asymmetric C-N bonds. In contrast to crystalline NQ, there is less pi-electron de-localization in crystalline TAG than in crystalline NQ. The C-N(1) bond is only elongated to 1.292(1) Å, and is significantly shorter than its two amino C-N(3) and C-N(5) bonds that are 1.373(1) Å and 1.381(1) Å, respectively. The intermolecular N-H...H hydrogen bonding in crystalline TAG is not strong enough to elongate either the imino C-N or the amino C-N bonds in the amidine moiety to the same extent as do the hydrogen bonds (N-H...O and N0H...N) in crystalline NQ.

Gilardi et al (ref. 11) reported that crystalline RDX had three pyramidal nitramino groups with N-N bonds that have bend angles of 19.9 deg, 33.3 deg, and 33.9 deg with N-N bond lengths of 1.351 Å, 1.392 Å, and 1.398 Å, respectively (table 6). The pyramidal conformation of these nitramino groups indicates sp^3 bonding.

The isolated NQ molecule has one planar N-N bond (1.352 Å) that is equivalent to the shortest crystalline RDX pyramidal N-N bond (1.351 Å), but it is shorter than the two remaining N-N bonds. However, upon crystallization of NQ, the N-N bond shortens to 1.334(2) Å, which is now shorter than the shortest N-N bond in crystalline RDX. The longer and weaker N-N bonds of RDX suggest that RDX should be more impact sensitive than NQ. The drop heights required for a 2 kg weight to set off RDX and NQ are 33 cm and >300 cm, respectively. This suggests that RDX actually is ten-fold more impact sensitive than NQ.

Although the difference in the N-N bond lengths predicts that RDX should be more impact sensitive than NQ, the differences in respective N-N bond lengths alone do not seem to justify the ten-fold greater impact sensitivity observed in the experiment. Hence, additional factors must contribute to the difference in sensitivity between the two energetic compounds.

The molecular packing and resultant intermolecular hydrogen-bond forces in crystalline NQ affect its macroscopic properties as well as its molecular geometry. To illustrate the effect of hydrogen bonding on properties, compare water (H_2O) with hydrogen sulfide (H_2S). The molecular weight of H_2) is 18 and is liquid at room temperature with a boiling point of 100°C. Yet, surprisingly, the heavier H_2S, with a molecular weight of 34 is a gas at room temperature and does not condense to liquid until –60.7°C. The reason for this apparent anomaly is that liquid H_2O has a network of strong O-H....O hydrogen bonds, while H_2S has no hydrogen bonds.

Crystalline RDX has neither intra-molecular nor intermolecular hydrogen bonds to stabilize it. To further illustrate the effect of hydrogen bonding on other properties, RDX with a molecular weight of 222 melts at 204°C, while the lower molecular weight NQ (104) melts at 222°C.

CONCLUSIONS

1. The canonical from of nitroguanidine (NQ) is represented by two amino C-N single bonds and one shorter imino C-N double bond; however, it was experimentally determined that the imino C-N bond is actually longer than either one of the amino C-N bonds.

2. The geometry of an isolated molecule optimized with the ab initio method does not reflect the affects of crystal field effects.

3. The disparity between the observed bond-lengths of crystalline NQ and the calculated bond lengths (canonical form of NQ) is caused mainly by the infinite hydrogen bond network and to lesser extent by the van der Waals forces encountered when the molecules of NQ are packed in the crystal.

4. Scission of the N-N bond is probably the first step in the decomposition of nitramine/ nitrimine molecules. The longest RDX N-N bond is 0.058 Å longer than the N-N bond in NQ. RDX is, indeed, more impact sensitive than NQ, but this bond length difference does not seem to justify the ten-fold decrease in the impact sensitivity of NQ.

5. Intermolecular forces such as hydrogen bonding, as in the case of NQ, improve the stability of an energetic compound.

6. When designing new energetic molecules, the effects of molecular packing and possible hydrogen bonding must also be considered in order to predict the potential sensitivity and energy of target solid energetic compounds (bulk material).

RECOMMENDATIONS

1. A similar investigation should be pursued for other energetic molecules containing nitrate ester, nitramino, nitro and geminal nitro groups.

2. When designing a new molecule or modifying a known molecule, the molecular packing, crystal geometry, and possible hydrogen bond formation and their effect upon the properties of the target compound should be taken into account. Remember, we design the molecule, but shoot the bulk material.

3. To optimize stability, "active hydrogen atoms" should be incorporated in the molecule. Atoms are capable of forming hydrogen bonds with oxygen atoms and/or nitrogen atoms. To insure hydrogen-bond formation, substitution of hydroxyl, amino, and/or imino groups on the target energetic molecule could be considered and perhaps maximized.

Table 1
Crystallographic data*

Crystal system	Orthorhombic
Lattice type	f-centered
Space group	Fdd2 (#43)
Lattice parameters:	
a	17.6390(5) Å
b	24.8730(7) Å
c	3.5903(1) Å
$\alpha=\beta=\gamma$	90 deg
Volume	1575.19(7) $Å^3$
Radiation	MoKα (γ = 0.71070 Å)
Z	16 molecules
D_x	1.736 g/cm^2

*Data obtained from Molecular Structure Corp., The Woodlands, Texas.

Table 2
Atomtic coordinates and Beq/Biso

Atom	x/a	y/b	z/c	Beq/Biso
O(1)	0.32285(8)	0.01075(5)	0.3701(7)	3.51(3)
O(2)	0.42592(8)	0.02562(5)	0.0650(7)	3.92(4)
N(1)	0.3046(1)	0.17163(7)	0.4314(8)	3.67(4)
N(2)	0.24602(9)	0.09349(7)	0.5688(7)	2.97(3)
N(3)	0.36389(8)	0.09618(5)	0.2506(8)	2.57(3)
N(4)	0.36927(8)	0.04278(6)	0.2308(7)	2.56(3)
C(1)	0.30200(9)	0.11852(7)	0.4226(8)	2.46(3)
H(1)	0.341(2)	0.189(1)	0.34(1)	4.5(6)
H(2)	0.264(1)	0.1913(9)	0.554(8)	3.4(5)
H(3)	0.206(2)	0.113(1)	0.69(1)	4.5(6)
H(4)	0.244(1)	0.057(1)	0.533(9)	4.3(6)

Table 3
Hydrogen bond lengths in angstroms (Å) and bond angles in degrees (deg)
(Donor atom indicated by D and acceptor atom indicated by A)

D-H...A			D-A (Å)	D-H (Å)	H...A (Å)	A-H-B (deg)	Atom B symmetry
N(1)	H(2)	O(2)	2.953(3)	0.98(3)	2.53(2)	106(2)	¼-x, -¼+y, ¾+z
N(1)	H(2)	O(2)	2.962(3)	0.98(3)	1.99(3)	174(2)	-¼+x, ¼-y, ¾+z
N(2)	H(3)	N(3)	3.137(3)	0.91(2)	2.23(3)	176(2)	-¼+x, ¼-y, ¾+z
N(2)	H(4)	O(1)	3.040(2)	0.92(2)	2.34(3)	132(2)	-x, ½-y, ½+z
N(2)	H(4)	O(1)	2.594(2)	0.92(2)	1.91(3)	129(2)	x, y, z
N(1)	H(1)	O(1)	3.292(2)	0.85(3)	2.47(3)	165(2)	¼-x, -¼+y, -¼+z

Table 4
Comparison of x-ray bond data for crystalline NQ with theoretical**
bond data for isolated NQ molecule

Bonds	X-ray (Å)	Calc* (Å)	Angles	X-ray (deg)	Calc (deg)
C(1)-N(1)	1.322(2)	1.332	N(1)-C(1)-N(2)	119.3(2)	115.962
C(1)-N(2)	1.321(2)	1.357	N(2)-C(1)-N(3)	112.8(2)	113.852
C(1)-N(3)	1.372(3)	1.310	N(1)-C(1)-N(3)	127.9(2)	130.185
N(3)-N(4)	1.334(2)	1.352	N(2)-N(3)-C(1)	118.9(1)	119.802
N(4)-O(1)	1.247(2)	1.214	O(2)-N(4)-N(3)	115.2(1)	115.108
N(4)-O(2)	1.239(2)	1.185	O(1)-N(4)-N(3)	124.6(1)	121.777
			O(1)-N(4)-O(2)	120.1(1)	123.112
			C(1)-N(1)-H(1)	122(2)	115
			C(1)-N(1)-H(2)	119(1)	119
			H(2)-N(1)-H(1)	118(2)	120
			C(1)-N(2)-H(4)	115(2)	118
			C(1)-N(2)-H(3)	120(2)	119
			H(2)-N(2)-H(3)	124(3)	120

*SCF ab initio calculation with 6-31G** basis sets.

Table 5
C-N bonds in isolated guanidine and NQ molecules and crystalline NQ

Bond	Guanidine	NQ	Crystalline NQ
Amino C(1)-N(1)	1.383 Å	1.332 Å	1.322(2) Å
Amino C(1)-N(2)	1.385 Å	1.355 Å	1.321(2) Å
Imino C(1)-N(3)	1.260 Å	1.310 Å	1.372(3) Å
N(3)-N(4)	-----	1.335 Å	1.334(2) Å

Table 6
Comparison of N-N bond lengths and bend angles in the isolated NQ molecule, crystalline NQ, and crystalline RDX

Compound	Bend angle (deg)	N-N bond (Å)
RDX	19.9	1.351
RDX	33.3	1.392
RDX	33.9	1.398
Crystalline NQ	1.9	1.334(2)
Isolated NQ molecule	0.0	1.352

REFERENCES

1. Thiele, J., "Nitroguanidine," Liebigs Ann, 270, p. 16, 1892.

2 McKay, A. F.; Picard, J. P.; and Brunet, P. E., Canad. J. Chem., 29, p. 746, 1951.

3. Bryden, J. H; Burkardt; Hughes, E. W.; and Donohue, J., "The Crystal Structure of Nitroguanidine," Acta. Cryst., 9, p. 573, 1956.

4. Choi, C. S., "Refinement of 2-Nitroguanidine Structure by Neutron Powder Diffraction," Acta. Cryst., B37, p. 1955, 1981.

5. Bulusu, S.; Duley, R. L.; and Autera, J. R., "Structure of Nitroguanidine: Nitroamine or Nitroimine? New NMR Evidence from $_{15}$N-Labeled Sample and $_{15}$N Spin Coupling Constants," Magn. Reson. Chem., 25, p. 234, 1987.

6. HyperChem5.1 Tools for Molecular Modeling, Hypercube, Inc, 1115 NW 4th St., Ganesville, FL, 1996.

7. Bracuti, A. J., "Structure of 1,2,3-Triaminoguanidine (TAG)," Acta. Cryst., C42, p. 1889, 1986.

8. Bulusu, S., "The Structure of N-methyl-N-Nitroguanidine," Acta. Cryst., B37, p. 1543, 1981.

9. Vladimiroff, T., "An Ab Initio and Density Functional Study of Nitroguanidine," Proceedings of the 34th JANNAF Combustion Meeting, CPI Publication 662, Vol. 1, p. 261, 1997.

10. Caminiti, R.; Pieretti, A.; Bencivenni, L.; Ramando, F.; and Sanna, "Amidine NC(N)N Skeleton: Its Structure in Isolated and Hydrogen Bonded Guanidines from Ab Initio Calculations," J. Phys. Chem., 100, p. 10928, 1996.

11. Archibald, T. G.; Gilardi, R.; Baum, K.; and George, C., "Synthesis and X-Ray Crystal Structure of 1,3,3-Trinitroazetine," J. Org. Chem., 55, pp 2920-2924, 1990.

DISTRIBUTION LIST

Commander
Armament Research, Development and Engineering Center
U.S. Army Tank-automotive and Armaments Command
ATTN: AMSTA-AR-WEL-TL (2)
AMSTA-AR-GCL
AMSTA-AR-WEE (4)
AMSTA-AR-WEE-B (10)
Picatinny Arsenal, NJ 07806-5000

Defense Technical Information Center (DTIC)
ATTN: Accessions Division (12)
8725 John J. Kingman Road, Ste 0944
Fort Belvoir, VA 22060-6218

Director
U.S. Army Materiel Systems Analysis Activity
ATTN: AMXSY-EI
392 Hopkins Road
Aberdeen Proving Ground, MD 21005-5071

Commander
Soldier and Biological/Chemical Command
ATTN: AMSSB-CII, Library
Aberdeen Proving Ground, MD 21010-5423

Director
U.S. Army Research Laboratory
ATTN: AMSRL-CI-LP, Technical Library
Bldg. 4600
Aberdeen Proving Ground, MD 21005-5066

Chief
Benet Weapons Laboratory, CCAC
Armament Research, Development and Engineering Center
U.S. Army Tank-automotive and Armaments Command
ATTN: AMSTA-AR-CCB-TL
Watervliet, NY 12189-5000

Director
U.S. Army TRADOC Analysis Center-WSMR
ATTN: ATRC-WSS-R
White Sands Missile Range, NM 88002

Commander
Naval Air Warfare Center Weapons Division
1 Administration Circle
ATTN: Code 473C1D, Carolyn Dettling (2)
China Lake, CA 93555-6001

Chemical Propulsion Information Agency
ATTN: Accessions
10630 Little Patuxent Parkway, Suite 202
Columbia, MD 21044-3204

GIDEP Operations Center
P.O. Box 8000
Corona, CA 91718-8000